

Cleaner Water: It's Elementary

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	8A
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf
Period 7	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf

Volatile organic compounds (VOCs) are a class of chemicals that impart tremendous benefits when used under controlled circumstances in commercial and industrial settings, but that pose a serious health threat if released into the environment. VOCs can persist in the environment for long periods of time, and have been implicated in a variety of human ailments including cancer, reproductive failures, and adverse neurological effects. Government and industry groups have struggled to clean up soil and water contaminated by these compounds, but the methods developed to date all have severe limitations. Recently, researchers at the University of Arizona in Tucson and at the Oak Ridge National Laboratory (ORNL) in Tennessee have succeeded in dechlori-

nating a variety of VOCs in the laboratory using palladized iron (Pd/Fe). A private company, Terrapure Systems L.L.C. of Tucson, is now developing a Pd/Fe remediation technology, or PIRT, for commercial applications, and could have a system in place within a year's time.

Halogenated VOCs (HOCs), including trichloroethylene, perchloroethylene, and trichloroethane, have been used for decades as industrial cleaning solutions and general degreasing solvents. Until recently, there was little regulation of the disposal of these compounds. As a result, there are literally thousands of sites in the United States and elsewhere where groundwater and soil are contaminated by these compounds. These sites include chemical manufacturing plants and disposal areas, elec-

troplating and metal finishing shops, hangars and aircraft maintenance areas, storage tanks that leak chemicals such as gasoline that contain VOCs, radioactive and mixed-waste disposal areas, paint stripping and spray booth areas, pesticide and herbicide mixing areas, solvent degreasing areas, manmade lagoons and ponds, and vehicle maintenance areas.

Hundreds of VOCs have been produced for use in a variety of products, including gasoline, dry-cleaning solvents, and degreasing agents. When users dispose of these products improperly or when a spill occurs, VOCs can contaminate groundwater and drinking water supplies. Some VOCs have been proven to cause cancer after prolonged exposure, while others are considered possible cancer risks.

<http://www.shef.ac.uk/chemistry/web-elements/>

VOCs can also cause other health problems including damage to the lungs, kidneys, liver, blood-cell forming tissue, and the immune and nervous systems.

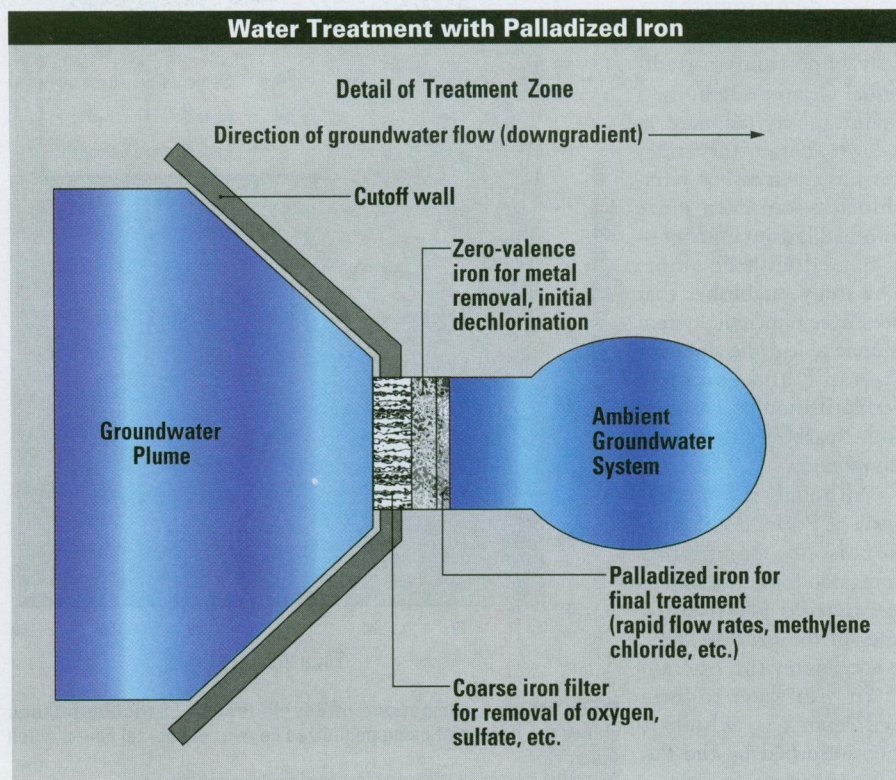
Currently, the technologies most commonly used to treat HOCs in groundwater, surface water, and leachate, according to the Federal Remediation Technologies Roundtable Web site, located at <http://www.frtr.gov/>, are air stripping and carbon adsorption. These are both *ex situ* technologies requiring groundwater extraction. Air stripping involves the mass transfer of volatile contaminants from water to air using a packed tower—a cylindrical structure filled with a packing material that serves as a VOC filter—or an aeration tank. Packed tower air strippers are set up either as permanent installations on concrete pads or as temporary installations on skids or trailers. This process is limited by high operating costs, the need for pretreatment of the water or periodic cleaning of the column where water hardness is high, and preheating of water to remove compounds with low volatility at ambient temperatures.

Liquid phase carbon adsorption technology requires groundwater to be pumped through a series of vessels containing activated carbon to which dissolved contaminants adsorb. When the adsorptive capacity of the carbon is reached, the carbon is either regenerated or removed for disposal. This technology is limited by high costs when used as the primary treatment on waste streams with high contaminant concentration levels. It is not applicable to sites having high levels of oily substances, and is not practicable where the water content of the hazardous substance is so high that frequent replacement of the adsorbent unit is necessary.

Research Using PIRT

Recognizing the limitations of existing technologies, researchers have been investigating new methods for the remediation of water and soils contaminated with VOCs and related compounds such as polychlorinated biphenyls (PCBs). Beginning in the early 1990s, researchers at the University of Waterloo in Toronto showed that elemental iron (Fe) could be used to dechlorinate many low-molecular-weight chlorinated hydrocarbons. However, Fe alone does not cause complete dechlorination of contaminants and has a prohibitively slow reaction rate for above-groundwater or air-treatment systems.

Elemental palladium (Pd) is a well-known catalyst of dechlorination reactions; therefore, researchers theorized that a bimetallic Pd/Fe system might prove to be



Mopping up with metals. A new decontamination process uses a palladized iron cassette in a permeable *in situ* barrier to remove a variety of volatile organic compounds from water.

Source: Oak Ridge National Laboratory, Environmental Technology Section, at <http://homer.hsr.ornl.gov/ets/palliron.html>.

more effective than Fe alone. In 1994, a team led by Quintus Fernando, a professor of chemistry at the University of Arizona, and Nic Korte, group leader of the Restoration Technology Group at the ORNL's environmental sciences division, pioneered the first experiments comparing Fe to a Pd/Fe system. The results have borne out their hypothesis.

The methodology employed by Fernando and Korte involves the deposition of Pd on Fe particles. The Fe is first acid-washed, then mixed in a solution of potassium hexachloropalladate, which serves to deposit Pd on the Fe surface. The resulting Pd/Fe bimetallic system is then rinsed in distilled water. A PCB solution is prepared, placed in a vial containing either Fe alone or Pd/Fe, then capped and shaken. Sample solutions are periodically withdrawn and analyzed by gas chromatography.

Seventy-two separate experiments were performed over a period of nine months with different batches of Pd/Fe containing varying ratios of Pd to Fe. The results were published in the November 1995 issue of *Environmental Science and Technology*. Through these experiments, Fernando and colleagues successfully dechlorinated all of the PCB congeners Aroclor 1254 and 1260 in approximately 5–10 minutes. The greater the amount of

Pd/Fe and the higher the percentage of Pd deposited on the Fe, the faster the reaction. The only reaction products of the dechlorination were relatively harmless biphenyl and chloride ions.

The researchers observed that the condition of the Fe surface plays an important role in the conversion of PCBs into biphenyl. Despite all attempts to remove the surface oxide layers, the Fe surface, when exposed to air and an aqueous solution, will form oxide layers in which the ratio of oxygen to Fe varies as a function of depth from the surface. The extent of the Pd deposited on this type of surface depends on the nature of these oxide layers and the porosity of the surface.

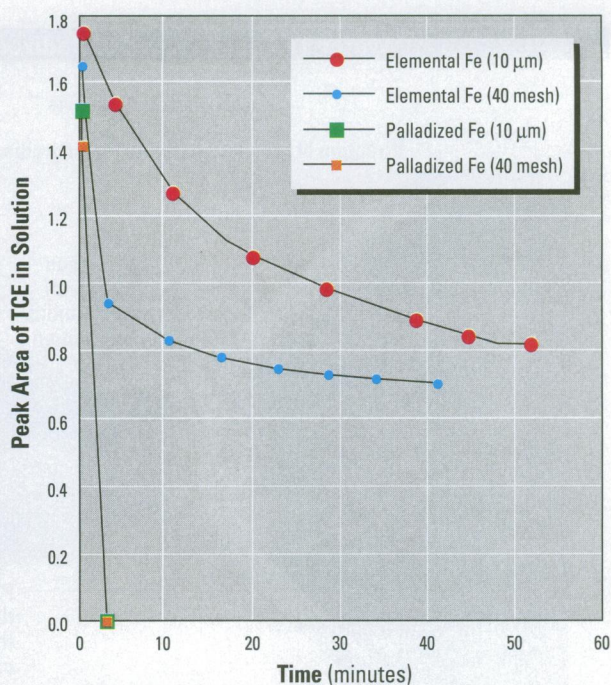
Also in 1994, Fernando, Korte, and the University of Arizona's Rosy Muftikian conducted experiments using Pd/Fe to dechlorinate various low-molecular-weight chlorinated hydrocarbons in water. Using a procedure similar to that employed with PCBs, the team's results, published in the October 1995 issue of *Water Research*, showed that they could completely dechlorinate all such compounds within 4–5 hours, most within a matter of minutes. The Pd/Fe process also successfully dechlorinated dichloromethane, a suspected carcinogen commonly found in paint strippers, metal degreasers, and propellants. Not

only is dichloromethane, which has proven particularly impervious to traditional cleanup methods, a significant contaminant in its own right, it is also what remains when carbon tetrachloride—an even more formidable contaminant—is treated with Fe alone. The study establishes that the Pd/Fe bimetallic system is preferable to Fe alone for the rapid and complete dechlorination of 1-carbon and 2-carbon chlorinated compounds.

Although the mechanism of Pd/Fe dechlorination is not completely understood, the researchers feel that Pd plays several roles in the process. First, it accelerates the reaction of Fe with water to form hydrogen gas, which is then adsorbed by the Pd. Subsequently, when a HOC contacts the bimetallic system, the gaseous hydrogen reduces the HOC to a halide and a halogenated-free organic compound. Fe in the bimetallic system is oxidized in the process.

"These findings are important, because if we can increase the rate at which contaminants will degrade, we can use less of the reactive media," says Bob Puls, senior research scientist with the EPA National Risk Management Research Laboratory in Ada, Oklahoma. "This, in turn, may allow us to decontaminate water sources lying deeper underground. Using a trenching system with iron alone, we are only able to decontaminate water *in situ* about 40 feet down. Many of the plumes we are dealing with lie deeper than that."

Puls says one of the drawbacks of PIRT is that the enhancement effect provided by Pd/Fe does not last as long as scientists would like. Currently, the U.S. Department of Energy Efficient Separations Program is



Quick clean. A comparison of dechlorination of trichloroethane shows the benefit of using palladized Fe over elemental Fe—a much faster rate.

Source: Oak Ridge National Laboratory, Environmental Technology Section, at <http://homer.hsr.ornl.gov/ets/palliron.html>.

funding the ORNL to further refine the technology for the treatment of PCBs and solvent waste at department sites. Korte, the principal investigator for this study, reports that he is testing different percentages of Fe—Fe pellets made with various binders—to develop the most rugged material possible and to minimize Pd and Fe losses while the material is being used.

Commercialization of PIRT

Capitalizing on the research done by the University of Arizona and the ORNL, Research Corporation Technologies (RCT) and Heritage Partners in Tucson formed Terrapure to further develop PIRT. RCT works in partnership with inventors and research institutions to identify, evaluate, protect, develop, and commercialize inventions. Heritage Partners is a consulting company specializing in environmental technology business develop-

ment, and has extensive experience in the development of adsorption and advanced oxidation environmental systems.

"The presence of halogenated organic compounds is widely recognized as a national and global problem with thousands of sites worldwide requiring remediation," says Donald Hager, president of Terrapure. "In this context, the potential opportunities for PIRT to make an impact appear substantial."

In terms of potential applications of PIRT, Hager says the system is proven to work with water, and that's where the technology will be applied first. He says there are limited data that the chemistry can be adapted to vapor phase contaminants. Direct application to soil is not foreseen, but PIRT can be applied to water/solvent/detergent mixtures used to clean soil. In fact, Hager says, PIRT is unique in its capacity to selectively dechlorinate organics in concentrated mixtures of waterborne organic contaminants.

With respect to decontamination of HOCs in groundwater, Hager says PIRT offers several advantages over the technologies in current use. The granular activated carbon technology accumulates HOCs on site, requiring frequent off-site disposal and ultimate destruction of the contaminants. Air stripping, meanwhile, simply transfers the contaminants from the water to the surrounding air.

"The long-term liability for future environmental or personal damages associated with off-site disposal remains with the original generator of the contaminants," Hager points out. "The on-site contaminant destruction offered by PIRT will assure immediate interest from industry, environmental engineers, and regulatory officials." Hager says it is too early to estimate the exact costs of PIRT, but he predicts it will be fully competitive with granular activated carbon, air stripping with contaminant destruction, and advanced oxidation systems.

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SUGGESTED READING

Grittini C, Malcolmson M, Fernando Q, Korte N. Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system. *Environ Sci Technol* 29(11):2898–2900 (1995).

Fernando Q, Korte N, Muftikian R. A method for the rapid dechlorination of low molecular weight chlorinated hydrocarbons in water. *Water Res* 29(10):2434–2439 (1995).